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**PRESENTATION OF MOLECULAR
PARAMETER VALUES FOR
INFRARED AND RAMAN
INTENSITY MEASUREMENTS**

(Recommendations 1988)

Prepared for publication by

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Presentation of molecular parameter values for infrared and Raman intensity measurements (Recommendations 1988)

Abstract - The field of basic and applied studies of infrared and Raman intensities is growing, and more experimental data as well as theoretical works are appearing in the scientific literature. The aim of the document is to point out where lack of common definitions and common use of dynamical and spectroscopic quantities may give rise to confusion among various authors. Recommendations are made as to the correct description of the sign of the various vibrational coordinates used, and of the eigenvectors derived from the dynamical matrix.

Studies of vibrational intensities in infrared and Raman spectroscopy have recently attracted the attention of an increasing number of workers (1). Knowledge of the wave-number dependence of the absorption coefficient in the infrared or scattering power of molecules in the Raman spectrum is increasingly important for applications which range from ordinary analytical chemistry through solid state physics all the way to astrophysics. At present such studies are conducted in laboratories all over the world, and the interest is both experimental and theoretical.

The theory attempts to correlate and organize the experimental results by interpretation based on quantum mechanical calculations or on models which try to find parameters to characterize experimental intensities in the same way that force constants have parametrized potential fields for the vibrational frequencies.

It is sometimes difficult to compare experimental data or theoretical predictions in the literature because of a lack of proper definition of the quantities used. Some of these quantities are considered here.

Infrared or Raman intensities of the i^{th} fundamental mode of vibration (designated I_i^{IR} or I_i^{Raman} , respectively) can be measured by the peak height of the absorption or scattering band, but are usually and more meaningfully measured experimentally by the integrated absorbance (taken to base e , either $\int \ln(I_0/I) d\nu$ or $\int \ln(I_0/I) d(\ln\nu)$, where the integral is taken over the i^{th} band (2)) or the corresponding expression of the scattering power I_i/I_0 (where I_i is the integrated radiant intensity for the i^{th} Raman band and I_0 is the incident radiance) for the Raman scattering. Whatever the experimental definition of the infrared intensity, it is proportional to the square of the theoretical matrix element for the transition moment $\langle 1|M|0\rangle$ obtained from theory by integrating the product of the excited state vibrational wavefunction, ψ_{1i} , times the result of operating on the vibrational ground state wavefunction ψ_{0i} by the vector dipole moment operator, M . The integration is made with respect to the vibrational coordinate Q_i , over all space. Similarly the intensity of the Raman scattering is proportional to $|\langle 1|\alpha|0\rangle|^2$, where α is the polarizability operator.

If the vibration is both electrically and mechanically harmonic, (the usual simplifying assumption for interpretation of data),

$$I_i^{\text{IR}} \sim \sum_u^3 |\partial M_u / \partial Q_i|^2 \quad \text{and} \quad I_i^{\text{Raman}} \sim \sum_{u,v}^3 |\partial \alpha_{u,v} / \partial Q_i|^2.$$

Here $\mathbf{M} = M_x \mathbf{i} + M_y \mathbf{j} + M_z \mathbf{k}$ is the molecular dipole moment, α is the molecular polarizability tensor, Q_i is the i^{th} normal coordinate and the summation is over all the components ($u = x, y, z$; $v = x, y, z$). The most important point to be made here is that the experimentally measured intensity is proportional to the square of the theoretically important intensity parameter ($\partial M_u / \partial Q_i$) or ($\partial \alpha_{u,v} / \partial Q_i$). Hence the experimental measured intensity does not determine the sign of these parameters. In the theoretical interpretation of intensities, the next step is usually to derive new parameters, such as those relating to bond or group motions, from the values of $\partial M_u / \partial Q_i$ by linear combinations of the latter. As a result, the values of these new parameters depend strongly on the choice of sign for each of the 3N-6 experimental values of $\partial M_u / \partial Q_i$ (or $\partial \alpha_{u,v} / \partial Q_i$). The determination of these signs is the primary problem in the interpretation of experimental vibrational intensities.

There are several methods for the determination of these signs, both by experimental studies and by approximate quantum mechanical calculations of these derivatives. However, the results from studies by different authors often cannot be compared because there had been no definition by the author either of the reference system of cartesian coordinates in which \mathbf{M} or α are described or of the phase of the normal coordinate Q_i . For this reason it is hereby recommended that the following conventions be adopted.

1. The coordinate systems used in the interpretation of the data must be clearly and explicitly defined.

The orientation of the cartesian axes system with respect to the molecule should be shown or described explicitly, as should the orientation of any permanent dipole moment.

In addition to the cartesian axes system, there are several other coordinate systems that must be defined. These include (3,4) the column vector of cartesian displacement coordinates \mathbf{X} , defined so that a displacement of atom i in the positive x direction Δx_i , for example, is positive; the column vector of internal displacement coordinates \mathbf{R} , the column vector of symmetry displacement coordinates \mathbf{S} and the column vector of the normal coordinates \mathbf{Q} . Here the internal displacement coordinates must be clearly defined. The sign convention for the out-of-plane bending and for the torsional coordinates must be specified explicitly, as pointed out in the IUPAC Recommendations on Definition and Symbolism of Molecular Force Constants (5).

The definition of the S_i elements as linear combinations of R_j elements, and the sign of S_i , must be reported explicitly. When two \mathbf{S} coordinates are degenerate, the definitions of the degenerate coordinates in \mathbf{S} or in a symmetrized \mathbf{X} matrix should be iso-oriented with cartesian axes which belong to the same irreducible representation.

When all of these coordinate definitions have been given, the phase of the normal coordinate is then defined by giving the eigenvector matrix \mathbf{L} :

$$\mathbf{R} = \mathbf{LQ}$$

$$\mathbf{S} = \mathbf{L}^S \mathbf{Q}$$

or

$$\mathbf{X} = \mathbf{L}^X \mathbf{Q}$$

2. All studies which deal with sign determinations of $\partial M_u/\partial Q_i$ or of $\partial \alpha_{u,v}/\partial Q_i$ should report the L matrix completely, in addition to the coordinate definition recommended in 1.

Notice that the ambiguities in the definition of the phase of Q_i arise from the fact that both L_i and $-L_i$ are column eigenvectors that solve the same secular equation with the same eigenvalues. Two solutions of the same problem may be obtained with opposite phases from two computing programs, even when exactly the same input data are used. From the viewpoint of dynamics the phase of Q_i is irrelevant, but this is not the case in intensity calculations.

3. If quantum mechanical calculations of intensity parameters are made by finite difference methods (for example $\partial M_u/\partial R_j \sim [M_u(\Delta R_j) - M_u^e]/\Delta R_j$), then it is very important to describe carefully exactly how the displacement was made.

These displacements (ΔR_j or ΔS_j) in a finite difference calculation should in principle be displacements corresponding to a purely vibrational motion, to give a displacement coordinate that is orthogonal to the pure translations and rotations of the molecule. The vibrational displacements satisfy the Eckart-Saytzev conditions (3,4). In that case the i^{th} element of the column vector of symmetrical cartesian displacements for each atom, X_j , is related to the column vector of symmetry displacement coordinates S by:

$$X_j = (A^S)_i S.$$

Here $(A^S)_j$ is the i^{th} row of the A^S matrix defined by:

$$A^S = \mathbf{m}^{-1} (B^S)^\dagger (G^S)^{-1};$$

\mathbf{m}^{-1} is the diagonal matrix of inverse atomic masses and the B^S and G^S matrices are defined in Ref. 3. (The " \dagger " designates the transpose of the B^S matrix.)

If S_i in a finite difference calculation is not defined in this way (or by some other equivalent method for satisfying the Eckart-Saytzev conditions) then the displacement coordinate mixes pure vibrational displacements with translational and rotational displacements and the so called "rotational corrections" (6) must be introduced in the interpretation of the calculated dipole derivative for infrared intensity calculations or of the calculated polarizability derivatives for Raman intensity calculations in the case of a non-spherical molecular polarizability tensor.

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